

**MICROCRYSTALS AND AMORPHOUS MATERIAL IN COMETS AND PRIMITIVE METEORITES: KEYS TO UNDERSTANDING PROCESSES IN THE EARLY SOLAR SYSTEM.** J. A. Nuth<sup>1</sup>, A. J. Brearley<sup>2</sup> and E. R. D. Scott<sup>3</sup>, <sup>1</sup>Astrochemistry Branch, Code 691 NASA's Goddard Space Flight Center, Greenbelt MD 20772 (nuth@gssc.nasa.gov), <sup>2</sup>Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque NM 87131, <sup>3</sup>HIGP, University of Hawaii at Manoa, Honolulu, HI 96822

**Introduction:** Comets, fine-grained matrices of chondrites, and chondritic interplanetary dust particles (IDPs) are each composed of both crystalline and amorphous silicates. The primitive solar nebula, in which comets and asteroids accreted, was formed from the collapsed core of a Giant Molecular Cloud, that, in turn, condensed from materials present in the interstellar medium (ISM). Despite observations that reveal the presence of crystalline magnesium silicate minerals in the shells of very high mass-loss-rate stars [1,2], typical silicate grains in the ISM are most likely to be amorphous, given their relatively long residence time in such a high radiation environment. An upper limit of ~3% crystalline grains can be derived from their non-detection in spectra of ISM solids [3].

If the vast majority of grains that enter the primitive solar nebula are amorphous, then the observation of crystalline dust in comets and primitive chondrite matrices indicates the action of specific processes required to transform the amorphous starting materials into the crystals that are observed. Below we discuss several examples of such processes.

**Crystalline Silicates in Comets:** One of the remarkable sets of observations made by the Infrared Space Observatory were studies of Comets Hale-Bopp and Hyakutake in the far infrared. Although Campins and Ryan [4] had postulated that crystalline olivine dust was present in the coma of Comet Halley, based on observations of fine-structure within the 10-micron silicate stretch, it was not until the observations of the phonon resonances of magnesium-rich silicate minerals in the far infrared that the idea of crystalline grains in comets was taken seriously. This idea contradicted models of comet formation that assumed that cometary materials had always been cold (<30K) or models of the ISM dust population that considered silicate grains to be amorphous (based on observational evidence).

This contradiction led to two hypotheses for the conversion of initially amorphous grains into the minerals observed in cometary comae. Nuth [5] and colleagues [6,7,8] suggested that evaporation and condensation processes produce large quantities of amorphous materials in the nebula and that these and the initially amorphous interstellar dust were annealed in the inner nebula, then transported outwards to the area of comet formation by an as yet undiscovered wind. Because comets begin aggregating at ~100 to 200 A.U.

[9] such winds may be observable with newer generation telescopes and instruments.

Shock waves, caused by matter falling into the giant planets, were also suggested as a means to convert amorphous dust to crystalline minerals [10]. This suggestion avoided the problems of an undiscovered outflow, but these events are extremely sporadic, and occur only once every 100,000 years. These two scenarios predict vastly different models for nebular chemistry. In the second scenario, the chemistry of the nebula is occasionally punctuated by a very brief period of high temperature reactions, but is otherwise a relatively quiescent gas, becoming progressively hotter and denser as it spirals to the sun. Only materials that are incorporated into a planetesimal-scale or larger body survive, and these bodies are formed from ice and dust grains that are modified from their interstellar starting compositions by reactions in the outer nebula.

The first scenario has vastly different implications for nebular chemistry. Although materials must still be preserved in planetesimal-scale bodies to survive, their chemistry is no longer limited to modifications that can be made to interstellar materials as the parcel of gas and dust falls to its 'final' orbital radius. Because a small fraction of the infalling material is transported back out into the far reaches of the nebula, the chemistry of the outer nebula can reflect processes that occur at much higher temperatures and pressures than previously assumed. As one example, higher pressures and temperatures can greatly increase the efficiency of surface-mediated reactions that convert CO, N<sub>2</sub> and H<sub>2</sub> into complex hydrocarbons such as those observed in comets [11]. Organic residues remaining on the surfaces of nebular grains could easily account for the highly refractory mixture of aliphatic and aromatic hydrocarbons found in carbonaceous meteorites [12].

**Crystalline and amorphous silicates in chondrite matrices:** Observations of matrices in primitive chondritic meteorites show that amorphous ferrous silicates and magnesian silicates were important components of the fine-grained dust in the solar nebula [13]. Rare, primitive, unaltered carbonaceous, CM2 and ordinary chondrites have matrices that contain a significant modal abundance of amorphous materials. This amorphous material occurs as compacted nanometer to  $\mu\text{m}$ -sized domains that act as a groundmass in which crystalline phases are embedded. The crystalline silicate component consists largely of magnesian olivines and

pyroxenes, including Mn-rich varieties [14]. Submicron olivines with varying FeO contents are also present in some [15,16] but not all [17] matrices. Distinct aggregates of crystalline grains with textures consistent with high temperature annealing also occur. Nanophase sulfide and metal particles are important components in these primitive chondrites in addition to trace amounts of presolar grains. Magnesian pyroxenes have intergrowths of monoclinic and orthorhombic structures (like those in chondrules) indicative of cooling from  $>1000^{\circ}\text{C}$  at  $\sim 1000^{\circ}\text{C/hr}$  [15,17]. Fine-grained FeO-rich olivines dominate the matrices of even mildly metamorphosed chondrites but are not nebular condensates, [e.g 18]. They formed by thermal and hydrothermal processing of amorphous nebular precursors within asteroids.

Primitive chondrite matrices share a number of characteristics with chondritic IDPs which are thought to come from comets [19]. These include the high abundance of amorphous materials, pyroxene structures indicative of rapid cooling and the presence of Mn-rich magnesian silicates. However, chondritic IDPs differ from the matrices of primitive chondrites in that grain sizes are smaller in IDPs, and presolar grains are more abundant (percent levels) [20-22].

In matrices of very weakly altered CM2 chondrites, most notably Y791198 [23], fine-grained rims consist largely of amorphous silicate material that has locally undergone partial hydration to form nanocrystalline phyllosilicates. Coarser-grained phyllosilicate phases, characteristic of more heavily altered CM chondrites are absent. Further, crystalline silicate phases of high temperature origin are extremely rare and consist of Mg-rich olivines, some of which are also Mn-rich. Distinct domains of sulfide-rich and sulfide-poor amorphous material are present on the submicron scale. These materials have many of the characteristics of the so-called granular units in IDPs [19].

**Implications for nebular processes:** Chondrite matrices and chondritic IDPs contain a mixture of materials with different formation mechanisms and thermal histories. The crystalline magnesian silicates, particularly micron to submicron defect-free, Mn-rich olivines, resemble forsterites in AOAs and may also be condensates, though inferred O-isotope differences suggest formation in different environments. Some magnesian silicates may also have formed from annealed amorphous material [24, 25]. The amorphous component of matrices could have a variety of origins. As discussed earlier, the bulk of silicate material entering the nebula was amorphous in character. Some component of this interstellar silicate material could have escaped thermal processing (evaporation or annealing) and been incorporated into chondrite matrices.

However, it seems improbable that this component is particularly voluminous [21,22]. Very limited oxygen isotopic data for matrices and bulk chondrite data suggest that chondrite matrices are  $^{16}\text{O}$ -poor, like chondrules, and formed in a similar environment to the chondrules themselves, i.e. represent materials that have been processed within the solar nebula. However, further oxygen isotopic data are needed to confirm this suggestion for more chondrite groups. If amorphous matrix materials did indeed form in the solar nebula, then they may represent material formed by disequilibrium condensation during short-lived high temperature events or by radiation-induced amorphization during, e.g. FU Orionis events or the T-Tauri phase of the protosun. Formation of amorphous smokes may occur during the short-lived high temperature events which formed chondrules. In such events, evaporation of some component of nebular dust must have occurred and this material must recondense under disequilibrium conditions, favoring formation of highly disordered silicate materials. As well as inducing evaporation, less energetic thermal events or the higher temperature regions of the inner nebula may have annealed amorphous materials to form the crystalline aggregates of Mg-Fe-silicates that occur in chondrite matrices. It may be that only the smallest single crystals of this material remained coupled to the gas for transport to the outermost nebula.

**References:** [1] Molster F.J. (2000) Ph.D. Thesis, University of Amsterdam. [2] Waters L.B.F.M. et al. (1996) *A&A*, 315, L245. [3] Li A. & Draine B.T. (2001) *ApJ*, 550, L213. [4] Campins H. & Ryan E.V. (1989) *ApJ*, 341, 1059. [5] Nuth J.A. (1999) LPS, XXX, #1726. [6] Nuth J.A. et al. (2002) *Met. Plan. Sci.*, 37, 1579-1590. [7] Nuth J.A. et al. (2000) *Nature*, 406, 275. [8] Hill H.G.M. et al. (2001) *Proc. Nat. Acad. Sci.*, 98, 2182-2187. [9] Weidenschilling S.J. (1997) *Icarus*, 127, 290. [10] Harker D.E. & Desch S.J. (2002) *ApJ*, 565, L109-112. [11] Kress M.E. & Tielens A.G.G.M. (2001) *Met. Plan. Sci.*, 36, 75-91. [12] Hill H.G.M. & Nuth J.A. (2003) *Astrobiology*, 3, 291. [13] Scott E.R.D. & Krot A.N. (2003) In *Treatise on Geochemistry* (eds, H.D. Holland & K.K. Turekian) 1, 143-200. [14] Klöck W. et al. (1989) *Nature*, 339, 126. [15] Brearley A.J. (1993) *GCA*, 57, 1521. [16] Alexander C.M.O'D. et al. (1989) *EPSL*, 95, 187. [17] Greshake A. (1997) *GCA*, 61, 437. [18] Weisberg M.K. & Prinz M. (1998) *MAPS*, 33, 1087. [19] Rietmeijer F.J.M. (1998) *Rev. Min.*, 36. [20] Messenger S. et al. (2003) *Science*, 300, 105-108. [21] Nguyen A.N. & Zinner E. (2004) *MAPS*, 39, A77. [22] Nagashima et al. (2004) *Nature*, 428, 921. [23] Chizmadia L.J. & Brearley A.J. (2003) *LPSC XXXIV*, #1419. [24] Hallenbeck S.L. et al. (1998) *Icarus*, 131, 198-209. [25] Hallenbeck S.L. et al. (2000) *ApJ*, 535, 247 – 255.